



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶: C08F 20/02, 20/62, B32B 27/00	A1	(11) International Publication Number: WO 95/09876 (43) International Publication Date: 13 April 1995 (13.04.95)
(21) International Application Number: PCT/US94/11216 (22) International Filing Date: 3 October 1994 (03.10.94) (30) Priority Data: 131,500 4 October 1993 (04.10.93) US P 43 41 815.5 8 December 1993 (08.12.93) DE (71) Applicants: BASF LACKE & FARBEN AKTIENGESELLSCHAFT [DE/DE]; Glasuritstrasse 1, D-48165 Münster (DE). MOBIL OIL CORPORATION [US/US]; 3225 Gallows Road, Fairfax, VA 22037-0001 (US). (72) Inventors: ENTHOVEN, Nicholas, Leonardus, Maria; Rembrandtstraat 42, NL-4003 KW Tiel (NL). LEMKE, Jurgen, Erwin; Langesteeg 7, NL-4011 JS Buren (NL). VAN RIJN, Peter, Eric; Wijnpeerweg 7, NL-4007 ZJ Tiel (NL). VAN SOMMEREN, Henricus, Petrus, Gemman; Langepas 2, NL-6658 DZ West Maas en Waal (NL). MCGEE, Dennis, E.; 7 Hillary Lane, Penfield, NY 14526 (US). TOUHSAGENT, Robert, Edward; 65 Valley Brook Drive, Fairport, NY 14450 (US). (74) Agents: ROBERTS, Peter, William et al.; Mobil Oil Corporation, 3225 Gallows Road, Fairfax, VA 22037-0001 (US).		(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, ES, FI, GB, GE, HU, JP, KE, KG, KP, KR, KZ, LK, LT, LU, LV, MD, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SI, SK, TJ, TT, UA, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: COLD SEALABLE COHESIVE POLYMERS (57) Abstract A copolymer preparable by the emulsion polymerisation of: a) at least one monomer which comprises an alkyl methacrylate having from 1 to 12 carbon atoms in the alkyl group; a vinyl aromatic; or a nitrile having ethylene unsaturation conjugated with the nitrile group, with at least one of the following: b) at least one copolymerisable soft monomer; and c) at least one copolymerisable functional monomer, the resulting copolymer having a glass transition temperature (T _g) from -35 °C to 50 °C and being formulatable into a coating which is cold sealable to itself under pressure but which has non-blocking characteristics.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

- 1 -

COLD SEALABLE COHESIVE POLYMERS

THIS INVENTION relates to cold sealable cohesive polymers; more particularly, this invention relates to copolymers preparable by emulsion copolymerisation; to their preparation; to cold sealable compositions containing them; to cold sealable structures comprising them; to sealed such structures; and to the use of such cold sealable compositions for coating plastics film.

Plastics packaging structures, such as plastics films, can be provided with adhesive coatings to enable an effective seal to be obtained. These coatings may be heat sealable coatings which are adhesive coatings sealable at elevated temperatures; or they may be cold sealable coatings which are sealable at a temperature from 0° to 40°C. In packaging comestibles, especially foodstuffs which are sensitive to heat (such as candy, chocolate and ice cream), the use of heated elements must be avoided to prevent spoiling of the packaged product.

Previous commercial cold sealable, pressure-sensitive coatings while not requiring the use of heated elements in the sealing process have high surface tack and a tendency to block.

This invention seeks to provide a polymer, formulatable to furnish a cold sealable, pressure-sensitive cohesive coating which is cohesive only when placed under pressure in contact with like coated surfaces and has low surface tack to, and does not block with, commercial acrylic-based coatings. The coatings need also to have good wetting ability, good coating uniformity and good seal strength on diverse substrates, including plastics film and paper; they should be sealable at as low as possible a temperature also to facilitate increased time speeds. Finally, the coatings should be free from objectionable odour; should be usable with foodstuffs; and have excellent optical properties, such as gloss.

According, therefore, to one aspect of this invention there is provided a copolymer preparable by the emulsion polymerisation, preferably aqueous emulsion polymerisation, of:

a) at least one monomer which comprises an alkyl methacrylate having from 1 to 12 carbon atoms in the alkyl group; a vinyl

aromatic; or a nitrile having ethylenic unsaturation conjugated with the nitrile group with at least one of the following: b) at least one copolymerisable soft monomer; and c) at least one copolymerisable functional monomer, the resulting copolymer having a glass transition temperature (T_g) from -35°C to 50°C and being formulatable into a coating which is cold sealable to itself under pressure but which has non-blocking characteristics.

Monomer (a) suitably comprises methyl methacrylate, ethyl methacrylate, propyl methacrylate, isopropyl methacrylate, n-butyl methacrylate, iso-butyl methacrylate, t-butyl methacrylate, n-pentyl methacrylate, isopentyl methacrylate, hexyl methacrylate, n-octyl methacrylate, 2-ethylhexyl methacrylate, decyl methacrylate, dodecyl methacrylate; styrene, an α -alkyl styrene, vinyltoluene; acrylonitrile or methacrylonitrile, especially methyl methacrylate or acrylonitrile.

Where monomer (a) comprises an alkyl methacrylate or a vinyl aromatic, this is suitably employed in an amount from 21 to 55%, such as from 30 to 45%, especially 35 to 42%, by weight, based on the total weight of monomer mixture. Where monomer (a) comprises a nitrile in addition to other monomers (a), the nitrile is suitably employed in an amount up to 25% by weight, preferably up to 10%, such as from 3 to 9%, by weight. However, where (a) solely comprises a nitrile it is suitably employed in an amount from 10 to 65% by weight, based on the total weight of monomer mixture.

Monomer (b) suitably comprises an alkyl acrylate having from 1 to 12 carbon atoms in the alkyl group; 1,3-butadiene; or a vinyl or vinylidene ester, preferably methyl acrylate, ethyl acrylate, propyl acrylate, isopropyl acrylate, butyl acrylate, isobutyl acrylate, t-butyl acrylate, n-pentyl acrylate, isopentyl acrylate, hexyl acrylate, n-octyl acrylate, iso-octyl acrylate, 2-ethylhexyl acrylate, decyl acrylate, 1,3-butadiene, vinyl acetate or vinylidene chloride, especially methyl acrylate or ethyl acrylate.

Monomer (b) is suitably employed in an amount from 30 to

85% by weight, suitably from 40 to 69% by weight, preferably from 48 to 60% by weight, based on the total weight of monomer mixture.

Monomer (c) suitably comprises an ethylenically unsaturated compound containing a carboxylic or a sulphonic acid group, desirably an α,β -ethylenically unsaturated carboxylic acid, preferably acrylic acid, methacrylic acid, itaconic acid, crotonic acid, maleic acid; or sulfoethyl methacrylate, especially acrylic acid or methacrylic acid.

Monomer (c) is suitably employed in an amount from 1 to 15%, such as 1 to 5%, by weight, preferably from 2 to 8% by weight, based on the total weight of monomer mixture.

In one aspect of the invention, it is preferred that the T_g of the copolymer is from -30°C to 15°C . Desirably, such a copolymer comprises from 10 to 65 wt.% of copolymerised monomer (a); from 30 to 85 wt.% of copolymerised monomer (b); and from 1 to 5 wt.% of copolymerised monomer (c), and has a number average molecular weight to 150000 (GPC). Preferably, such a copolymer has a number average molecular weight from 50,000 to 90,000.

In another aspect of the invention, it is preferred that the T_g of the copolymer is from 25°C to 50°C , preferably 30°C to 50°C . Desirably, such a copolymer comprises from 30 to 55 wt.% of polymerised monomer (a) 40 to 69 wt.% of polymerised monomer (b); and from 1 to 15 wt.% of polymerised monomer (c). Preferably, such a copolymer has a number average molecular weight in the range 8,000 to 12,000 (GPC against a polystyrene standard and dissolved in tetrahydrofuran).

In general, the amount of each monomer will depend on the desired glass transition temperature of the copolymer of the invention. This is related as follows :

$$\frac{1}{T_g} = \frac{W_{fa}}{T_{ga}} + \frac{W_{fb}}{T_{gb}} + \frac{W_{fc}}{T_{gc}}$$

where:

T_g represents the glass transition temperature of the copolymer of the invention;

W_i represents the weight fraction of monomer (i); and

T_{gi} represents the glass transition temperature of a homopolymer of monomer (i).

The TABLE below gives representative T_g

<u>TABLE</u>	
<u>Monomer (a)</u>	<u>T_g (°C)</u>
Acrylonitrile	97
<u>Monomer (b)</u>	
Ethyl acrylate	-22
Hexyl acrylate	-57
Isopropyl acrylate	-3
Iso-octyl acrylate	-85
Butyl acrylate	-54
Methyl acrylate	8
Vinylidene chloride	-17
Isobutyl acrylate	-43
1,3-Butadiene	-78
Vinylacetate	-32
<u>Monomer (c)</u>	
Acrylic acid	106
Methacrylic acid	185
Itaconic acid	---
Sulfoethyl methacrylate	---
Maleic acid	---
Crotonic acid	---

It has been found that lower glass transition temperatures, typically less than 3°C, more typically less than 0°C and even more typically about -5°C, exhibit better pressure sealable properties, but this can vary depending upon the comonomers used. The mean diameter of the polymer particles is generally from 0.05 to 0.3 microns.

The acid numbers of the copolymer of the invention is typically from 10 to 100 mg KOH/g.

It may be desirable that the copolymer of this invention is crosslinked. Low levels, usually less than 5% by weight, of a crosslinking agent, such as divinylbenzene or 1,3-butylene glycol dimethacrylate, or, indeed, any other crosslinking agent known in the art may be employed.

It is found that the desired effect of the chain transfer agent to lower the average molecular weight of the copolymer could be countered by the effect of the crosslinking agent; therefore, when higher levels of crosslinking agent are used, higher levels of the chain transfer agent are usually used and vice versa. This helps to balance the properties of cohesive strength and sealability.

This invention, in another aspect, also provides a process for the preparation of a copolymer as herein defined, which process comprises (a) mixing at least one monomer (a) with at least one of monomers (b) and (c) in relative proportion so that the resulting copolymer has a T_g from -35°C to 50°C ; and (b) polymerizing the monomers under emulsion polymerization conditions.

Copolymers of the present invention may typically be prepared by an emulsion polymerization process in known apparatus; for example in a stirred reactor with heating and cooling means. Any of the herein defined monomers, and their relative proportions, may be utilised. The polymerization may be effected in the presence of water, an emulsifying agent and a catalyst which may be a free radical catalyst or a redox system.

The procedure for charging the reactor may comprise forming a solution of all the monomers; the water; the emulsifier; and the catalyst. As an alternative, a portion of the catalyst may initially be charged and the remainder added, slowly, during the polymerization. It is also possible initially to charge a portion of the water and of the emulsifier and to prepare from the remainder and from the monomer mixture a preemulsion which is added slowly at the polymerization temperature, the catalyst again being initially charged separately or a portion thereof being added separately. It is also possible to add the monomer

mixture in a first stage in the form of a preemulsion and in a second stage to add the monomer mixture in bulk, i.e. without water and emulsifier, and to add the catalyst separately but in parallel therewith. It is preferred initially to charge solution of water and emulsifier and slowly to add the monomer mixture and, separately therefrom but in parallel therewith, the catalyst in water, at the polymerization temperature. Subsequently, after renewed addition of emulsifier, in the second polymerization stage the remainder of the monomer mixture is metered into the reactor. The remainder of the catalyst, which was not charged initially, can also be added completely after the addition of the monomers. However, this subsequent metered addition of catalyst is less advantageous.

Advantageously, the quantitative ratio of monomers to water is selected such that the resulting dispersion of acrylate copolymer has a solids content from 20 to 40%.

Typical catalysts include hydrogen peroxide; benzoyl peroxide; inorganic persulfates such as ammonium or potassium persulfate; inorganic perphosphates such as ammonium or potassium perphosphate; organic peresters such as perisopivalates. Redox systems require a combination of such oxidants with a water soluble reductant; for example sulfur compounds such as alkali metal bisulfites, thiosulfates or hydrosulfites; ascorbic acid; triethylamine; hydrazine; hydroxylamine; glycolic acid; or tartaric acid. Generally, the total amount of catalyst employed may be from 0.1% by weight to 2% by weight based on the total weight of the monomer.

The emulsion polymerization may typically be carried out in the presence of one or more anionic, nonionic or cationic emulsifiers; for example, alkyl carboxylic acid salts, phosphoric acid salts, alkyl sulfate salts, alkyl sulfonate salts, alkyl aryl ether alcohols and alkyl aryl polyether sulfate salts. More particularly, examples of anionic emulsifiers include alkali metal or ammonium salts of sulfuric acid monoesters of alkylphenols or of alcohols; sulfuric acid monoesters of ethoxylated alkylphenols or ethoxylated alcohols; or phosphoric esters of alkoxyated alkylphenols. Examples of

emulsifiers utilised include alkali metal salts of sulfuric acid monoesters of nonylphenol reacted with 23 mol of ethylene oxide per mole, alkyl- or arylsulfonate, sodium lauryl sulfate, sodium lauryl ethoxylate sulfate and the alkali metal salt of diesters of sulfosuccinic acid with alcohols having 6 to 20 carbon atoms. The nonionic emulsifiers which are preferably used are ethers of nonylphenols reacted with 5 to 23 mol of ethylene oxide. It is preferred to employ phosphates of alkoxyated alkylphenols, especially phosphates of the reaction product of 1 mol of nonylphenol with 5 mol of ethylene oxide, having an acid number of 125. Generally, the total amount of emulsifier employed may be from 0.01 to 2.0 percent by weight based on the total amount of water.

The polymerization may be conducted in a redox system or in a higher temperature thermal process using a persulfate-type initiator or an azobisisobutyronitrile initiator.

In general, the polymerization may be carried out a temperature from 40°C to 100°C, suitably from 70°C to 90°C, preferably 60°C to 80°C, at a pressure from 101 to 308 kPa (0 to 30 psig). A thermal polymerization may be carried out at the higher range of these temperatures typically above 70°C. The reaction may be conducted in glassware with a reflux condenser. This stage is usually carried out in the presence of an inert gas, such as nitrogen. The polymerization is generally carried out for a time from 1 to 8 hours, preferably 3 to 4 hours. After completion of the polymerization reaction, the pH of the polymer can be adjusted up to 10, more specifically, from 6 to 10.

A two-stage polymerization process is also contemplated.

In the first stage of the emulsion polymerization, from 5 to 20% by weight of the monomer mixture may be polymerized at a temperature from 70 to 90°C. In the second stage of the polymerization, preferably after further addition of emulsifier, the remaining 80 to 95% by weight of the monomer mixture is polymerized in the presence of the polymer obtained in the first stage of the emulsion polymerization.

The resulting acrylate copolymer of the invention is at

least partially neutralized by the addition of bases, and, if desired, conventional auxiliaries and additives for the production of the aqueous sealing coating are added. The bases employed are ammonia and/or amines, advantageously in the form of an aqueous solution of the neutralizing agent. Ammonia is particularly preferred. Generally, the second stage polymerization may be performed under the same temperature and pressure conditions as in the first stage. A preformed seed latex is made in the first stage to which up to 95% of the remaining amount of monomer feed is gradually fed in a second stage over a period from 2 to 5 hours. The total reaction time of the second stage may usually be from 4 to 6 hours.

Examples of suitable chain transfer agents which may be included in the emulsion polymerization process of the invention include mercaptans; polyhalogen compounds; and branched aromatic hydrocarbons such as isooctyl thioglycolate, thioglycerol, dodecylmercaptan or trimethylbenzene. Usual amounts are from 0.1 to 5% by weight based on the weight of total monomer and the chain transfer agent is preferably employed at all stages of the emulsion polymerization.

In one embodiment of the invention there is a two-stage polymerization in which the seed, or core, latex comprises up to 50 wt.% of a different polymer such as a polymer described in U.S. Patent No. 5,070,164. To this is added, as the remaining monomer feed, a monomer feed of this invention.

After drying, the resulting latex formulation of the copolymer of this invention adheres to packaging film substrates even after exposure to moisture. That is, they retain a significant amount of their original bond strength even after immersion in water. Once solidified by drying, the coated surface does not adhere to non-treated, uncoated film surfaces such as untreated polypropylene or acrylic-based surface coatings.

This invention further provides a cold sealable composition comprising a polymer as herein defined.

A cold sealable composition of the invention may comprise any of the copolymers of the invention. The composition may be

- 9 -

an aqueous solution or dispersion of the copolymer, suitably with a solids content from 20 to 40 wt.%, and may contain suitable auxiliaries and additives as are conventional in seal-coating. These include antiblocking additives; hydrophobicizing agents; slip additives; and antifoaming additives. The hot-slip properties can be improved by the addition of solid, finely divided, water-insoluble inorganic materials, for example colloidal silica. Suitable antiblocking additives are finely dispersed minerals and finely divided waxes and wax-like materials which melt at temperatures above the maximum temperatures occurring during storage of sealable structures comprising them and which are not soluble in the copolymer of the invention at these temperatures. Examples of natural waxes are paraffin wax, microcrystalline wax, beeswax, carnauba wax, Japan wax and montan wax; examples of synthetic waxes are hydrogenated castor oil, chlorinated hydrocarbon waxes and long-chain fatty acid amides. The abovementioned waxes also lead to an improvement in the cold-slip properties of the coated plastics films, which should be understood as the ability of the films to slip over surfaces at room temperature.

The present invention also provides a sealable structure comprising a substrate coated on a surface thereof with such a cold sealable composition; and a sealed such structure containing perishable goods.

Before applying a cold sealable composition of the invention to a substrate, such as a plastics film, to form a sealable structure of the invention, the surface of the film is generally pretreated in order to ensure that the coating adheres firmly to the substrate. This treatment is carried out in accordance with known procedures; for example, by chlorinating the plastics film substrate; by oxidizing it with agents such as chromic acid or hot air; by steam treatment; by corona discharge; or flame treatment. The pretreatment used is preferably flame treatment or high-voltage corona discharge.

After being pretreated, the or each surface of the substrate is generally precoated with a primer that helps to anchor the topcoat in order to ensure the adhesion of the

- 10 -

coating to the substrate film. Appropriate precoating agents, or primers, are known from the literature and include, for example, alkyl titanates; epoxy-type primers; melamine-formaldehyde and polyethyleneimines. The latter are particularly suitable for precoating plastics films as in polystyrene latex which contains at least one epoxy functionality. In this context, the polyethyleneimines can be applied to the optionally pretreated plastics films either from organic or from aqueous solution. In this case the concentration of the polyethyleneimine in the aqueous or organic solution may be, for example, 0.5% by weight. Suitable polyethyleneimine primers are described in, for example, DE-A-24 40 112 and US-A-3,753,769.

The uncoated plastics films generally have a thickness of from 0.015 to 0.060 mm. The aqueous sealing coating is applied to the plastics film in a conventional manner, for example by gravure application, roller application, dipping, or spraying with the aid of the intaglio or flexographic printing process or the reverse-roll application process. The excess aqueous solution can be removed by squeeze rollers or draw-off blades. The sealing coatings should conventionally be applied in a quantity such that, during drying, a smooth, uniformly distributed layer having a weight of from 1 to 4 g/m² is laid down.

The coating formed by the sealing coating on the plastics film is subsequently dried with hot air, radiated heat or by means of any other conventional means. It is not necessary to apply the release coating layer which is necessary when using cold-sealing coatings.

The low adhesion to commercial acrylic-based coatings of the cold sealable composition of this invention is an important feature of the invention because these coatings impart the combined properties of machinability and printability to untreated and release-treated polypropylene. The untreated and release-treated polypropylene, while being machineable, is not printable. The latex coating presents a smooth, non-tacky surface which will not block to acrylic-based surface coatings

- 11 -

under normal operating conditions. However, if similarly coated surfaces are placed in contact with each other, under pressure, and at an elevated temperature up to 66°C (150°F), at room temperature or even at below room temperatures; for example 16°C (60°F), then the coated surfaces become cohesive forming a strong bond between each other. With certain polymers, the bond created has been found to be stronger than the film itself. The seal temperature required can be affected by the thickness of the composition on the substrate; that is, thicker substrates can require higher temperatures for pressure sealability.

Thus, the cold sealable compositions of the present invention are very useful in imparting high cold seal bond strength to packaging film substrates, particularly polyolefin film, such as polypropylene film substrates. Substrates which are particularly contemplated for use with these cold sealable compositions to provide sealable structures of the present invention include olefin polymers, such as case or oriented polypropylene, coextruded films, nylon, white opaque film, cellophane, paper, polyesters, high density polyethylene and linear low density polyethylene.

The polymeric portion of the contemplated acrylic based coatings should contain at least 80 wt.% acrylic, preferably greater than 90 wt.% acrylic. Small amounts of other materials such as acrylonitrile and ethylene acrylic acid can also be present in the acrylic-based polymer, typically less than 10 wt.%. The amount of non-acrylic materials should be limited as they can cause blocking. The acrylic-based coating can be formulated with particles such as polyethylene, silicon and silicone, silica, talc, or other particles from 0.5 to 3.0 microns.

Commonly known techniques can be employed to apply the emulsion polymer formulation of the present invention to the film or paper substrate. For example, when impregnating or saturating the substrate, it may be dipped or sprayed. If the substrate is coated, this may be accomplished by dipping, spraying or by employing a roller, spreading knife, brush or the like. Generally, for the best crimp sealability, the emulsion

polymer formulation should be applied at a low level, typically, applied in an amount of from about 0.5 to 5 g per 6,500 sq. cm. (1000 sq. in.), preferably about 1 to 1.5 g per 6,500 sq. cm. to the film substrate.

The emulsion polymerization formulation of the present invention may be compounded with, or have mixed therein, other known ingredients or stabilizers, antifoaming agents, dying adjuvants, pigments, waxes, corn starch, silica, talc and the like other compounding aids to control surface tack and other surface properties. Thickeners or bodying agents may be added to the polymers so as to control the viscosity of the polymer and thereby achieve the proper flow properties for the particular application desired.

The sealing temperature at which a sealed structure according to the invention is fabricated is generally above ambient temperature. In general it is from 20°C to 80°C, preferably at least 30°C and particularly preferably from 40°C to 70°C. Sealing occurs with the application of temperature and pressure. During the application of pressure, the sealing coatings are brought into contact in such a way that they become matted together. The pressures applied are generally from 5-30 bar, preferably from 6-8 bar. Sealing times of from a few 1000ths of a second up to a few 10ths of a second are generally adequate. The dry weight of the sealing coating in the film coating is in general from 1 to 4 g/m².

The sealed structures, for example, packaging containers, produced according to the invention have outstanding properties with respect to their adhesion to the substrate and to their sealed-seam strength. The latter is preferably at least 250 g/2.54 cm. The sealing coatings are particularly suited to containing perishable goods, especially heat-sensitive comestibles and conform to current foodstuffs regulations and are stable in terms of odor. The coatings do not block with respect to untreated plastics films, for example oriented polypropylene. Despite the very good antiblocking properties, the sealing temperature is distinctly below the range of sealing temperatures which is usual for heat-sealing coatings. In

general, the sealing temperature is about 30°C lower than is conventional with current sealing coatings.

The sealed packaging containers produced by the process according to the invention have excellent sealed-seam strengths and excellent optical properties. The coated plastics films have excellent antiblocking properties, i.e. they do not become stuck on contact with uncoated plastics films. In addition, it is particularly advantageous that sealing can be carried out at relatively low temperatures. The sealing temperature is generally from 20 to 30°C lower than the sealing temperature when using conventional heat-sealing coatings. This enables the line speed, at the same sealing temperature, to be increased. A further advantage is that the release coating on the other side of the film, which is required when using conventional cold-sealing coatings, is not absolutely necessary in the process according to the invention.

Preferred plastics films are polyolefin films, for example polyethylene and polypropylene films. These films are particularly preferably of polypropylene, especially oriented polypropylene.

In a further aspect, the present invention also provides the use of a cold sealable composition as herein defined for coating a plastics film.

The following Examples illustrate the invention; parts are by weight unless stated otherwise.

EXAMPLE 1

This Example relates to the preparation of an acrylate emulsion (AE 1) for use as an aqueous sealing coating.

31.1 parts of demineralized water and 0.05 part of an anionic emulsifier (ester type) were weighed into a reaction vessel. The initial charge was heated at 80 to 82°C. A mixture of 16.2 parts of methyl acrylate, 11.9 parts of methyl methacrylate, 1.4 parts of acrylic acid, 0.5 parts of isooctyl thioglycolate and 0.4 part of water was then weighed into the monomer tank and premixed. 0.09 part of ammonium peroxodisulfate and 0.3 part of demineralized water were added. 10% of the contents of the monomer tank were metered uniformly

into the reactor over the course of 30 min at approximately 80°C. Subsequently, 0.8 part of the anionic emulsifier was added.

The reaction mixture was maintained at the reaction temperature for 10 min, and then the remaining contents of the monomer tank were metered in uniformly over a period of 3 hours at 80°C. Subsequently the batch was polymerized for 2 hours at 80°C. Then, at a temperature of 60°C, a mixture of 0.6 parts of ammonia (25% strength) and 6.0 parts of water was added with stirring. The batch was subsequently adjusted, using a mixture of ammonia (25% strength) and water (mixing ratio 0.6:6.0), to a solids content of 30% and a viscosity of 30 mPa.s at 25°C. The content of ammonia (100%) in the finished coating (solids content 30%) was 0.15 parts.

The resulting acrylate copolymer had a number-average molecular weight M_n of 10,000, an acid number of 37 mg of KOH/g and a glass transition temperature (T_g) of 42°C (measured by differential scanning calorimetry (DSC)).

EXAMPLE 2

This Example relates to the preparation of an acrylate emulsion (AE 2) for use as an aqueous sealing coating.

20.8 parts of demineralized water and 0.03 part of an anionic emulsifier (ester type) were weighed into a reaction vessel. The initial charge was heated at 80 to 82°C. A mixture of 10.8 parts of methyl acrylate, 7.9 parts of methyl methacrylate, 0.9 part of acrylic acid, 0.3 part of isooctyl thioglycolate and 0.2 part of water were weighed into the monomer tank and premixed. A solution of 0.06 part of ammonium peroxodisulfate in 0.3 part of demineralized water was added to the initial charge. 10% of the contents of the monomer tank were metered uniformly into the reactor over a period of 30 min at approximately 80°C. 0.56 part of the anionic emulsifier was then added.

The reaction mixture was maintained at the reaction temperature for 10 min, and then the remaining contents of the monomer tank were metered in uniformly over a period of 3 hours

- 15 -

at 80°C. Subsequently the batch is polymerized for 2 hours at 80°C. A mixture of 1.6 parts of ammonia (25% strength) and 42.5 parts of water were weighed into a dilution vessel and heated to 70°C. The reactor contents were drained off over 45 min at 70°C.

EXAMPLE 3

This Example relates to the preparation of an acrylate emulsion (AE 3) for use as an aqueous sealing coating.

An acrylate emulsion AE 3 was prepared by analogy with the preparation of AE 1, using :

- 1.86 parts of acrylic acid
- 4.30 parts of methyl methacrylate
- 23.34 parts of ethyl acrylate
- 0.79 parts of ammonia (25% strength) and
- 5.81 parts of water.

The resulting acrylate copolymer had a number-average molecular weight (GPC) of 10,000, an acid number of 49 mg of KOH/g and a glass transition temperature (T_g) of 4°C (DSC).

EXAMPLE 4

This Example relates to the preparation of an acrylate emulsion (AE 4) for use as an aqueous sealing coating.

An acrylate emulsion AE 4 was prepared by analogy with the preparation of AE 1, using :

- 1.86 parts of acrylic acid
- 3.15 parts of acrylonitrile
- 24.49 parts of ethyl acrylate
- 0.79 parts of ammonia (25% strength) and
- 5.81 parts of water.

The resulting acrylate copolymer had a number-average molecular weight (GPC) of 10,000, an acid number of 49 mg/KOH/g and a glass transition temperature (T_g) of 5°C (DSC).

EXAMPLE 5

This Example relates to the preparation of an aqueous sealing coating (ASC).

200 parts of AE 1 were taken. 18.0 parts of a commercially

- 16 -

available 25% strength emulsion of carnauba wax (MICHEMLUBE (trade mark) 160 ex. Michelman, USA) were added slowly with stirring and homogeneously dispersed by further stirring for 5 minutes to provide ASC 1.

EXAMPLE 6

This Example relates to the preparation of an aqueous sealing coating (ASC 2).

200 parts of AE 3 were taken. 79.60 parts of a commercially available colloidal silica paste (LUDOX (trade mark) AM) were added with stirring and homogeneously dispersed by further stirring. Adding ammonia is appropriate, the pH of the sealing coating was adjusted to a value between 7.2 and 7.5.

EXAMPLE 7

This Example relates to the preparation of an aqueous sealing coating (ASC 3).

200 parts of AE 4 were taken. 0.59 part of SYLOID (trade mark) ED 3 (5% strength dispersion in water) and 30 parts of a commercially available, colloidal silica paste (LUDOX AD 30) were added with stirring and homogeneously dispersed by further stirring. Adding ammonia if appropriate, the pH of the sealing coating was adjusted to a value between 7 and 8.

EXAMPLE 8

This Example relates to the application of the sealing coatings ASC 1 to 3.

The coatings were applied using a doctor blade to a polyethyleneimine-primed, oriented polypropylene film 29MB210 from Mobil Plastics Europe, Belgium. The application weight was 1.5 ± 0.2 g/m². The coated film was dried in a HELIOS (trade mark) laboratory oven for 15 s at a max. surface temperature of 95°C.

These coated films were used to determine the coefficient of friction and the blocking resistance with respect to the coated or uncoated reverse of the film. In addition, the sealed-seam strength was determined. The measured results are

shown in Table 1.

Coefficient of friction

The coefficient of friction was determined using the ALTEK (trade mark) 9505A device, within a period of 30 min after application of the sealing coatings, in the application direction.

The blocking resistance was tested in 2 ways:

- 1.) 24 hours at 47°C, 0.5 kg/cm²

Test coating against uncoated outer face

- 2.) 24 hours at 47°C, 0.5 kg/cm²

Test coating against acrylic-coated outer face.

Assessment took place on the basis of the separation effect, the rating 0 denoting the complete absence of any blocking while the rating 5 indicates total blocking.

Sealed-seam strength

Two 25 mm wide strips of the above-described coated polypropylene films were sealed at a sealing temperature of less than 80°C and a sealing pressure of 5 bar. In each case the sealed-seam strength was determined using the TESTOMETRIC (trade mark) 100 D device from H. Messmer, London, at a speed of 300 mm/min and a measured width of 25 mm. The results are given in TABLE 1.

TABLE 1

	ASC 1	ASC 2	ASC 3
Coefficient of friction	0.010	0.030-0.060	0.06-0.12
Blocking resistance			
uncoated face	0.5	0.5	0.5
acrylic-coated face	0.5	1	1
Sealed-seam strength			
(g/25 mm)	300-400	300-400	138*

* Sealed-seam strength after sealing at room temperature.

EXAMPLE 9

This Example relates to the preparation of an acrylic emulsion (AE 5) and an aqueous sealing coating (ASC 4) of the

invention.

Using a semi-continuous batch process, a latex was prepared by continuously adding an metering 404 g. of the total monomer feed over a period of 2.5 hours to a reactor containing 475 g of water, 1 g of 30% sodium lauryl sulfate, as emulsifier, and 1.6g 70% tert-butyl hydroperoxide, as free-radical catalyst. The premixed total monomer feed comprised of 80.2 wt.% ethyl acrylate, 15.8 wt.% acrylonitrile, 3 wt.% methacrylic acid, and 1 wt.% isooctyl thioglycolate (as a chain transfer agent), based on the total monomer feed. A feed containing 7g of 30% sodium lauryl sulfate, 0.7g of sodium formaldehyde sulfoxolate (as a catalyst activator) and 45g water was added over a three hour period. The emulsion polymerization reaction was maintained at 60°C to 70°C and the reaction was performed in an atmospheric pressure reactor equipped with a reflux condenser and in the presence of inert nitrogen gas. Sufficient agitation was used to uniformly disperse the monomers in the reactor. The reactor batch was held for about 1 hour after the addition of all the feeds.

After polymerization, the terpolymer was blended with a typical combination of wax and talc.

The latex was subsequently cooled and filtered through a 200 mesh screen. The latex stability of the resultant EA/ACN/MAA terpolymer was excellent.

EXAMPLE 10

This Example relates to the preparation of a crosslinked polymer (AE 6). The procedure of this example was substantially the same as that of Example 9 except that it was a thermally-initiated polymerization. Using a semi-continuous batch process, a latex was prepared by continuously adding and metering 406 g of the total monomer feed over a period of 2.5 hours to a reactor containing 475 g water, 1 g of 30% sodium lauryl sulfate, as emulsifier, and 12 g of 10% aqueous ammonium persulfate, as a free radical initiator that was prepared immediately prior to the start of the polymerization and added to the reactor approximately two minutes prior to beginning the addition of the monomer feed. The pre-mixed total monomer feed

- 19 -

79.8 wt.% ethyl acrylate, 14.8 wt.% acrylonitrile, 3 wt.% methacrylic acid, 1 wt.% divinyl benzene (85% pure), and 1.5 wt.% iso-octyl thioglycolate, as chain-transfer agent, based on the total monomer feed. A feed containing 9 g of 23% sodium dodecyl benzene sulfonate, as stabilizing emulsifier, and 41 g water was then added over a 3-hour period. The emulsion polymerization reaction was maintained at 75 to 85°C and the reaction was performed in the same laboratory glassware that was used in Example 9. After all feeds were in, the batch was held at 80°C for 1 hour at which time 17 g of 30% aqueous ammonia (diluted to 400 g with water) was added. When the temperature again reached 80°C, the batch was held an additional hour at 80°C and then cooled and removed from the glassware.

The properties of the polymers prepared by Examples 9 and 10 are summarized in TABLE 2 below:

TABLE 2
Characteristics of Polymer Latex

	<u>Example 9</u>	<u>Example 10</u>
Latex		
Total Solids (%)	42.8	31.5
Particle Size (nm)	130	87
pH	6.1	9.5

EXAMPLE 11

Polymer latex formulations prepared in accordance with the emulsion polymerization process of both Examples 9 and 10 were applied by direct gravure to the sealable portions of one side of a standard acrylic coated 92 gauge oriented polypropylene film primed with polyethyleneimine (which helps to anchor the topcoat to the substrate). The other side of the film was primed with the polyethyleneimine and coated with an all-acrylic polymer formulation. The coatings were dried at a temperature of 220°F.

The coating weights for both pressure sealable coatings were 1.2 (+/- 0.4) g/1000 sq. in. while the coating weight for the acrylic-based coating was 0.6 g/1000 sq. in.

The properties of the coated films were tested and the results of the testing, in comparison with the results of testing a cold sealable terpolymer described in U.S. Patent No. 5,070,164, made by a 1-step polymerization process, are summarized in TABLE 3.

TABLE 3
Results On Cold Seal Coatings

Adhesive	Chemical Composition	Ratio	Calculated Tg (°C)	Crimp Seal (g/in)	Block to Standard Acrylic	Surface Tack
One-Stage Emulsion polymerized polymer	EA/VA/MAA	67/30/3	-5	375*	BTD	low
Emulsion polymerized polymer of Example 9	EA/ACN/MAA	81/16/3	-5	357	21	low
Emulsion polymerized polymer of Example 10	EA/ACN/MAA/DVB	81/15/3/1	-5	458*	27	low

Base Film: Standard 92 Gauge Acrylic Coated oriented polypropylene film
Crimp: 80 psi, 1/2 sec., room temp.

ACN = Acrylonitrile
EA = ethyl acrylate
MAA = methyl methacrylate
MAA = methacrylic acid
BTD = block to destruction
DVB = divinylbenzene

* This crimp seal was strong enough to tear the film which indicates a good seal; that is, the adhesive was stronger than the base film. In general, however, good crimp seal strength is usually over 200g/in, typically over 300 g/in.

- 22 -

CLAIMS

1. A copolymer preparable by the emulsion polymerisation of :

- a) at least one monomer which comprises an alkyl methacrylate having from 1 to 12 carbon atoms in the alkyl group; a vinyl aromatic; or a nitrile having ethylene unsaturation conjugated with the nitrile group.

with at least one of the following:

- b) at least one copolymerisable soft monomer; and
c) at least one copolymerisable functional monomer,

the resulting copolymer having a glass transition temperature (T_g) from -35°C to 50°C and being formulatable into a coating which is cold sealable to itself under pressure but which has non-blocking characteristics.

2. A copolymer according to claim 1 wherein the monomer (a) comprises methyl methacrylate, ethyl methacrylate, propyl methacrylate, isopropyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, t-butyl methacrylate, n-pentyl methacrylate, isopentyl methacrylate, hexyl methacrylate, n-octyl methacrylate, 2-ethylhexyl methacrylate, decyl methacrylate, dodecyl methacrylate; styrene, an α -alkyl styrene, vinyltoluene; acrylonitrile or methacrylonitrile.

3. A copolymer according to claim 1 or 2 wherein the monomer (b) comprises an alkyl acrylate having from 1 to 12 carbon atoms in the alkyl group; 1,3-butadiene; or a vinyl or vinylidene ester.

4. A copolymer according to claim 3, wherein the monomer (b) comprises methyl acrylate, ethyl acrylate, propyl acrylate, isopropyl acrylate, butyl acrylate, isobutyl acrylate, t-butyl acrylate, n-pentyl acrylate, isopentyl acrylate, hexyl acrylate, n-octyl acrylate, iso-octyl acrylate, 2-ethylhexyl acrylate, decyl acrylate, 1,3-butadiene, vinyl acetate or vinylidene

chloride.

5. A copolymer according to any preceding claim wherein the monomer (c) comprises an ethylenically unsaturated compound containing a carboxylic or a sulphonic acid group.

6. A copolymer according to claim 5 wherein the monomer (c) comprises acrylic acid, methacrylic acid, itaconic acid, crotonic acid, maleic acid; or sulfoethyl methacrylate.

7. A copolymer according to any preceding claim, wherein the glass transition temperature is from -30°C to 15°C .

8. A copolymer according to claim 7 which comprises from 10 to 65 wt.% of copolymerised monomer (a); from 30 to 85 wt.% of copolymerised monomer (b); and from 1 to 5 wt.% of copolymerised monomer (c).

9. A copolymer according to any preceding claim which has a number average molecular weight from 50,000 to 90,000.

10. A copolymer according to any preceding claim 1 to 6 wherein the glass transition temperature is from 25°C to 50°C .

11. A polymer according to claim 10, which comprises from 30 to 55 wt.% of polymerised monomer (a) 40 to 69 wt.% of polymerised monomer (b); and from 1 to 15 wt.% of polymerised monomer (c).

12. A polymer according to claim 11, which has a number average molecular weight in the range 8,000 to 12,000.

13. A copolymer according to any preceding claim which has been crosslinked.

14. A process for the preparation of a copolymer according to claim 1, which process comprises :

- 24 -

- (a) mixing at least one monomer (a) with at least one of monomers (b) and (c) in relative proportion so that the resulting copolymer has a Tg from -35°C to 50°C; and
- (b) polymerizing the monomers under emulsion polymerization conditions.

15. A process according to claim 14 wherein the respective monomers, and their relative proportions, are defined in any of claims 1 to 6, 8, 11 or 13.

16. A process according to claim 14 or 15, which is carried out in the presence of water, an emulsifying agent and a polymerization catalyst.

17. A process according to claim 14, 15 or 16, wherein the polymerization is carried out at a temperature of 40°C to 100°C at a pressure from 0 to 30 psig (101 to 308 kPa).

18. A process according to claim 14, 15, 16 or 17, wherein the polymerization is carried out in a two stage process.

19. A process according to claim 18, wherein the first stage of the polymerization process is carried out at a temperature from 70°C to 90°C with a total of 5 to 20 wt.% of the total monomer mixture; and the second stage of the polymerization process is carried out at a temperature from 70°C to 90°C in the presence of the polymer obtained in the first stage, together with the remaining 80 to 95 wt.% of the monomer mixture.

20. A process according to claim 19, wherein after the second stage polymerization the resulting polymer is at least partially neutralised by the addition of a base.

21. A process according to any of claims 14 to 20,

wherein the polymerization is carried out in the presence of a chain transfer agent.

22. A process according to any of claims 14 to 21 wherein at least one additive is added during or after step (a) or step (b) of the process, the additive being a stabiliser, antifoaming agent, drying adjuvant, pigment, wax or thickener.

23. A cold sealable composition comprising a polymer according to any of claims 1 to 13.

24. A cold sealable composition according to claim 23 comprising an aqueous solution or dispersion of said polymer.

25. A cold sealable composition according to claim 24, wherein the solids content of the aqueous solution or dispersion is from 20 to 40 wt.%.

26. A sealable structure comprising a substrate coated on a surface thereof with a composition according to any of claims 23 to 25.

27. A sealable structure according to claim 26, wherein the substrate is coated on another surface with an acrylic-based composition.

28. A sealable structure according to claim 27, wherein the substrate comprises a layer of an olefin polymer, a nylon, a polyester or paper.

29. A sealable structure according to claim 26, 27 or 28 wherein the or each surface of the substrate is pre-coated with a primer.

30. A sealed structure comprising a coated substrate defined in any of claims 26, 27, 28 or 29 and containing perishable goods.

- 26 -

31. A sealed structure according to claim 30 wherein the goods are heat-sensitive comestibles.

32. Use of a cold sealable composition according to any of claims 23 to 25 for coating a plastics film.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US94/11216

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C08F 20/02, 20/62; B32B 27/00

US CL :Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 526/318.4, 329.1, 328.4, 329.5, 329.7, 330, 343; 428/511, 516, 522

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS: cohesive and cold seal?

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 5,070,164 (MIN ET AL) 03 December 1991, see entire document.	1-4, 14-16
X	US, A, 4,403,464 (DUNCAN) 13 September 1983, see entire document.	1-4
--		-----
Y		1-4, 14-16
X	US, A, 4,000,359 (WATTS ET AL) 28 December 1976, see col. 1, line 51 to col. 3, line 8.	1-4, 14-16
--		-----
Y		1-4, 14-16
X	US, A, 2,790,735 (McLAUGHLIN ET AL) 30 April 1957, see col. 1, line 59 to col. 4, line 55.	1-4, 14-16

☒ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:	*T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be part of particular relevance	*X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
E earlier document published on or after the international filing date	*Y*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Z*	document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means		
P document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

09 DECEMBER 1994

Date of mailing of the international search report

13 FEB 1995

 Name and mailing address of the ISA/US
 Commissioner of Patents and Trademarks
 Box PCT
 Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

PAUL R. MICHL

Telephone No. (703) 308-2351

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/11216

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 3,696,082 (SMITH) 03 October 1972, see entire document.	1-4, 14-16

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US94/11216

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 5-13, 17-32
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐
☐

The additional search fees were accompanied by the applicant's protest.

No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US94/11216

A. CLASSIFICATION OF SUBJECT MATTER:

US CL :

526/318.4, 329.1, 328.4, 329.5, 329.7, 330, 343; 428/511, 516, 522